AD-A230 182

CRREL

SPECIAL REPORT 90-38

(2)

Development of a Simplified Field Method for the Determination of TNT in Soil

Thomas F. Jenkins

November 1990

For conversion of SI metric units to U.S./British customary units of measurement consult ASTM Standard E380, Metric Practice Guide, *published by the American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103.*

This report is printed on paper that contains a minimum of 50% recycled material.

Special Report 90-38

U.S. Army Corps of Engineers
Cold Regions Research & Engineering Laboratory

Development of a Simplified Field Method for the Determination of TNT in Soil

Thomas F. Jenkins

November 1990

Prepared for
USA TOXIC AND HAZARDOUS MATERIALS AGENCY
REPORT CETHA-TS-CR-90125

PREFACE

This report was prepared by Dr. Thomas F. Jenkins, Research Chemist, Geochemical Sciences Branch, Research Division, U.S. Army Cold Regions Research and Engineering Laboratory (CRREL). Funding for this research was provided by the U.S. Army Toxic and Hazardous Materials Agency, Aberdeen Proving Ground, Maryland (R-90, Multi-Analytical Services), Martin H. Stutz, Project Monitor.

Marianne E. Walsh of CRREL and Dr. C.L. Grant, Professor Emeritus, University of New Hampshire, are acknowledged for technical review of this manuscript, and Patricia Schumacher for conducting several initial feasibility tests. Kathlene Koehler, Marianne Walsh and Paul Miyares are also acknowledged for technical assistance.

A special acknowledgment is given to Capt. Craig Myler and Jim Arnold of USATHAMA, and Dr. Richard Williams of Weston Corporation, who assisted in the field test of this method at Umatilla Army Depot, Umatilla, Oregon.

CONTENTS

ILLUSTRATIONS

TABLES

Table | Page

Development of a Simplified Field Method for the Determination of TNT in Soil

THOMAS F. JENKINS

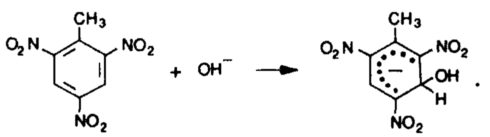
INTRODUCTION

Recently, Jenkins and Schumacher (1990) evaluated a field kit for the determination of TNT in water and soil. This kit was originally developed by Heller et al. (1982) as a field tool to detect low concentrations of TNT in water and its use was later extended to TNT in soil extracts (Erickson et al. 1984). A discussion of the mechanism of detection as well as an evaluation of the performance of this kit was presented elsewhere (Jenkins and Schumacher 1990). In general, however, the kit provides a means for detecting the presence of TNT in soil, but does not allow precise or accurate estimation of concentration. It is also somewhat difficult to use under field conditions* and requires access to electrical power, which limits its usage under field conditions.

Evaluation of the kit indicated that a much simpler approach was possible, relying on the same chemical reactions and colorimetric detection. Initial tests showed this approach to be sufficiently sensitive for field use, and the following discussion is a result of subsequent research directed at assessing this possibility.

BACKGROUND

As early as 1891, Janovsky observed that colored reaction products were formed when polynitroaromatic compounds reacted with alkali such as potassium hydroxide. Meisenheimer (1902) and Jackson and Earle (1903) independently arrived at similar chemical structures to explain this phenomenon and the quinoidal structures they proposed for these highly colored species are now known as Jackson–Meisenheimer anions; eq 1 shows the production of the anion from 2,4,6-trinitrotoluene (TNT):

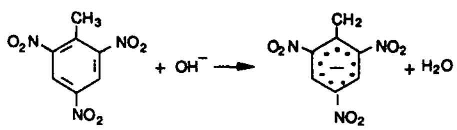


(1)

* Personal communication with C. Myler, USATHAMA, 1990.

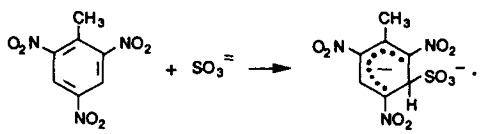
The specific colors that are visually observable for various dinitro- and trinitroaromatic compounds were presented by Bost and Nicholson (1935). In general, Jackson–Meisenheimer anions for dinitroaromatics are blue to purple while those from trinitroaromatics are red.

In addition to the formation of the classical Jackson–Meisenheimer anions by addition of a base to the 3-position on the TNT ring, a second type of anion can result from base abstraction of a proton from the methyl group of TNT (eq 2). According to Terrier (1982), the classical Jackson–Meisenheimer anion is produced from TNT more rapidly, while the product of reaction 2 is more thermodynamically stable:



(2)

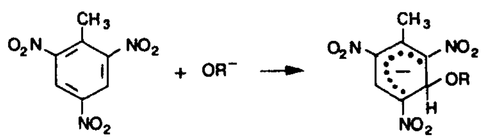
When the sulfite ion is present along with hydroxide, addition of sulfite to the aromatic ring can also occur (Terrier 1982) as shown in eq 3:



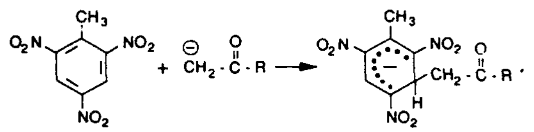
(3)

This anion apparently fades more slowly than that formed from hydroxide alone (Ruchhoft and Meckler 1945) with stabilities extended from about 30 minutes for the hydroxide complex (Kay 1941) to at least six hours (Ruchhoft and Meckler 1945).

When the base-catalyzed reaction takes place in either an alcohol or ketone solution (Janovsky reaction), addition of the alkoxide (eq 4) or the carbanion (eq 5) can also result (Hall and Poranski 1970):



(4)

 (5)

These reactions have been used analytically for a number of applications and a few examples are given below. Baernstein (1943) describes a method for the determination of benzene and toluene in certain commercial organic solvents by nitration of the aromatic rings with fuming nitric acid, followed by addition of a base to form the Jackson–Meisenheimer anions. Detection and quantitation of the colored anions is obtained using a spectrophotometer at 560 nm.

Ruchhoft and Meckler (1945) describe a method to determine TNT concentrations in water and sewage. Their method involves addition of hydroxide and sulfite to the aqueous solution with spectrophotometric determination at 460 and 505 nm.

Kay (1941), also using the Jackson–Meisenheimer anions, developed a field method for the determination of TNT in air. He trapped the TNT by bubbling the air through acetone and then added a concentrated sodium hydroxide solution to generate the colored anions. He quantified the TNT concentration by visual comparisons of the color intensity to standards and quoted a detection limit (in solution) of about 4 mg/L.

Yinon and Zitrin (1981) present a number of other forensic applications of this type of reaction for detecting nitroaromatics in post-blast debris.

OBJECTIVE

The objective of the research described here is to develop a simple, rapid field method to estimate TNT concentrations in soil. The chemicals and equipment needed should be usable under field conditions by analysts with only minimal chemical expertise. If possible, the method should not require electrical power, so that measurements can be made at the site of potential pollution. The method should be rapid enough to allow decision makers the ability to utilize the results on site to make judgments regarding the need to take additional samples for laboratory analyses or, under a cleanup scenario, continue or halt soil excavation.

EXPERIMENTAL

Analytical standards

Analytical standards for TNT, 1,3,5-trinitrobenzene (TNB) and methyl-2,4,6-trinitrophenylnitramine (tetryl) were prepared from Standard Analytical Reference Material (SARM) obtained from the U.S. Army Toxic and Hazardous Materials Agency (USATHAMA), Aberdeen Proving Ground, Maryland. The SARMs were dried to constant weight in a vacuum desiccator in the dark, and stock standards were prepared in Baker HPLC grade acetonitrile.

Test solutions of 2,4-dinitrotoluene (2,4-DNT), 2,6-dinitrotoluene (2,6-DNT), 1,3-dinitrobenzene (DNB), p-nitrotoluene (p-NT), o-nitrotoluene (o-NT), m-nitrotoluene (m-NT), nitrobenzene (NB), nitroglycerine (NG), pentaerythritol tetranitrate (PETN), 2,4,6-trinitrophenol (picric acid), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) were also prepared from SARM. Test solutions for 2-amino-4,6-dinitrotoluene (2-AmDNT) and 4-amino-2,6-dinitrotoluene (4-AmDNT) were prepared from material obtained from Dr. D. Kaplan, Natick Laboratories, with confirmation of identities by GC/MS analysis. The test solution for 1,3-dinitrophenol was prepared from technical grade material from Baker. Its identity was also confirmed by GC/MS.

Test solutions were prepared in either Type I reagent grade water, Baker HPLC grade methanol or Baker HPLC grade acetone. Soil extraction in the laboratory used HPLC grade solvents. Soil extraction for the field test of the method utilized commercial grade acetone obtained at a hardware store in Umatilla, Oregon.

Soils

Soils used for laboratory extraction studies included field-contaminated and uncontaminated soils from a number of present and former military installations in 10 different states.

Certification testing of the method was conducted using USATHAMA standard soil. Interference tests utilized a commercial potting soil obtained locally that was rich in humus and soils from military installations that were negative for munitions as determined by RP-HPLC. Soils for the field test were collected from a dry disposal lagoon at Umatilla Army Depot, Umatilla, Oregon.

Spectrophotometers

Two spectrophotometers were used to measure absorbance at various wavelengths in the visible region of the spectrum. A Coleman Junior II (Model 6/20) spectrophotometer (bandpass 20 nm) was used for most laboratory tests. Subsequent field measurements were made with a Hach DR/2 spectrophotometer (bandpass 17 nm) operated in the battery-powered mode.

Generation of Jackson–Meisenheimer anions

A pellet of potassium hydroxide (KOH) and about 0.2 g of sodium sulfite were added to 20–25 mL of solutions of TNT. Solutions were manually shaken for

3 minutes then filtered through a Millex-SR filter unit into a cuvette. Absorbance was read at 540 nm.

RESULTS AND DISCUSSION

Initial feasibility tests

An initial feasibility test was conducted to determine if the color intensity for the Jackson–Meisenheimer anion from TNT was sufficiently strong to allow detection and concentration estimation at criteria levels. Criteria levels are site specific, but have been established at 5 μg/g for TNT at two sites that have been subjected to cleanup by soil incineration (Rosenblatt 1986).

For the first test, solutions of TNT in methanol were used since methanol was the solvent of choice for the indicator tube field method. After reaction with KOH and sodium sulfite, the maximum molar absorptivity of the TNT anion was only about 4.3×10^3 L cm^{-1} mole^{-1}. The ability to detect TNT at the criterion level would be possible, but variable background color from humic material in the soil extracts would make detection problematical.

Early studies (Bost and Nicholson 1935, Baernstein 1943) tended to employ acetone rather than methanol for generation and measurement of these Jackson–Meisenheimer anions. An accidental use of acetone instead of methanol in a subsequent test revealed that molar absorptivities for the TNT anions produced in acetone (eq 5) were greater by a factor of four than TNT anions in methanol. This additional sensitivity was judged to be quite useful and subsequent tests were conducted with acetone. Acetone is also an excellent solvent for TNT, as can be seen in Table 1, and hence it should be a much better soil extraction solvent than methanol. It is also available with adequate purity at

Table 1. Solubility of TNT in various solvents.

Solvent	*TNT solubility (g/100 g at 20°C)*
Water	0.013 (a)
Carbon disulfide	0.48 (a)
Carbon tetrachloride	0.65 (a)
Ethyl Alcohol (95%)	1.23 (a)
Trichloroethylene	3.04 (b)
Diethylether	3.29 (a)
Aniline	8.1 (a)
Methanol	9.5 at 40°C (b)
1,2-Dichloroethane	18.7 (b)
Chloroform	19 (a)
Chlorobenzene	33.9 (b)
Toluene	55 (a)
Benzene	67 (a)
Acetone	109 (a)
Pyridine	137 (a)

a—Taylor and Rinkenbach (1923).
b—U.S. Army (1984).

hardware stores throughout the United States, which precludes the need to ship solvent to field sites. It is, however, somewhat more volatile and hence should be used with care due to increased flammability.

Absorbance spectra of analyte anions in acetone

A 2.1-mg/L solution of TNT was prepared in 95% acetone–5% water and the Jackson–Meisenheimer anions were generated as usual. The absorbance spectrum from 400 to 600 nm was then obtained on a Hach spectrophotometer (Fig. 1). Two absorbance maxima (λ_{max}) were observed at about 462 and 540 nm, the molar absorptivities being 2.70×10^4 and 1.77×10^4 L m^{-1} mole, respectively. This solution was visually red.

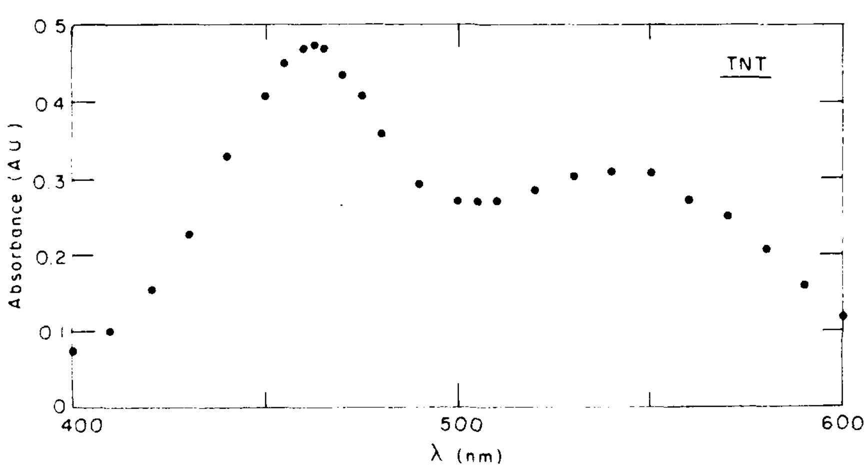


Figure 1. Visible absorbance spectrum of TNT anion in acetone.

Table 2. Colors and λ_{max} obtained for acetone solutions of compounds treated with KOH and sodium sulfite.

Compound	Color observed: This study	Color observed: Bost and Nicholson (1935)	λ_{max} (400–600 nm)
Nitrobenzene	None	None	—
o-nitrotoluene	None	None	—
m-nitrotoluene	None	None	—
p-nitrotoluene	None	None	—
1,3-dinitrobenzene	Purple	Purplish-blue	570
2,4-dinitrotoluene	Blue	Blue	570
2,6-dinitrotoluene	Pinkish-purple	——	550
1,3,5-trinitrobenzene	Red	Red	460, 560
Tetryl	Orange	—	460, 550
2-amino-DNT	Pale Yellow	—	400
4-amino-DNT	None	—	—
Nitroglycerine	None	—	—
PETN	None	—	—
RDX	None	—	-
HMX	None	—	—
Picric Acid		Reddish-Orange	420
2,4-dinitrophenol		Yellowish-orange	430
TNT	Red	Red	462, 540

A number of other nitroaromatics, nitramines, nitrate esters and polynitrophenols were tested under similar conditions and the visible spectrum of their anions obtained. The visual color observed and the λ_{max} obtained for each are given in Table 2. Absorbance spectra for 1,3,5-trinitrobenzene, tetryl, 2,4- and 2,6-DNT, and 1,3-dinitrobenzene are shown in Figures 2–6.

Clearly several other polynitroaromatics and polynitrophenols also give colored anions under these conditions. The anions from TNB would be very difficult to distinguish from TNT anions, although TNB, a phototransformation product of TNT, is generally present at much lower concentrations in explosive residues than TNT. Tetryl will also give anions that would be difficult to distinguish from TNT and, in the past, tetryl was used in conjunction with TNT in an explosive called Tetratol. Thus, if TNT and tetryl or TNT and TNB are present in the same residue, tetryl or TNB will produce a positive interference with TNT determination. During site cleanup activities, however, the ability to detect tetryl or TNB as well as TNT may be quite useful.

Effects of variable concentrations of water in acetone extracts

Extraction of field soils with acetone will result in extracts containing variable concentrations of water, depending on the moisture content of the soil at the time of sampling. Moisture contents of soils vary over a wide range, depending on a variety of factors including par-

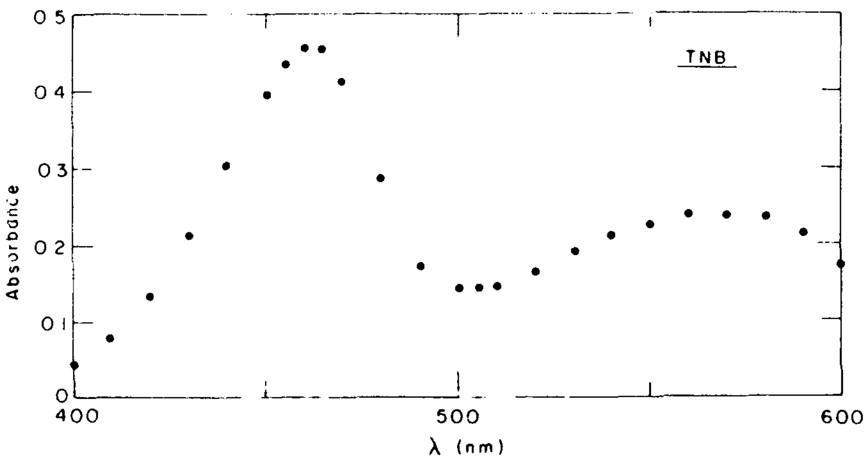


Figure 2. Visible absorbance spectrum of TNB anion in acetone.

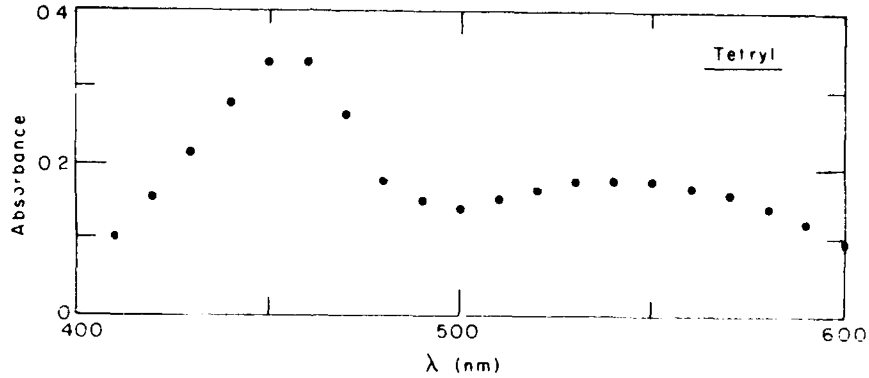


Figure 3. Visible absorbance spectrum of anion from tetryl in acetone.

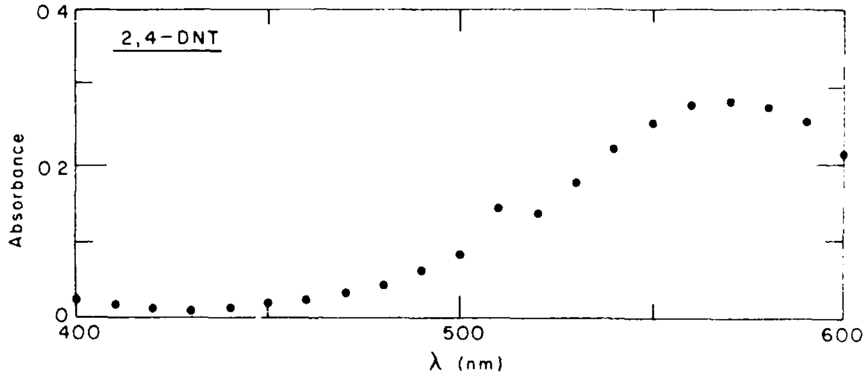


Figure 4. Visible absorbance spectrum of anion from 2,4-DNT in acetone

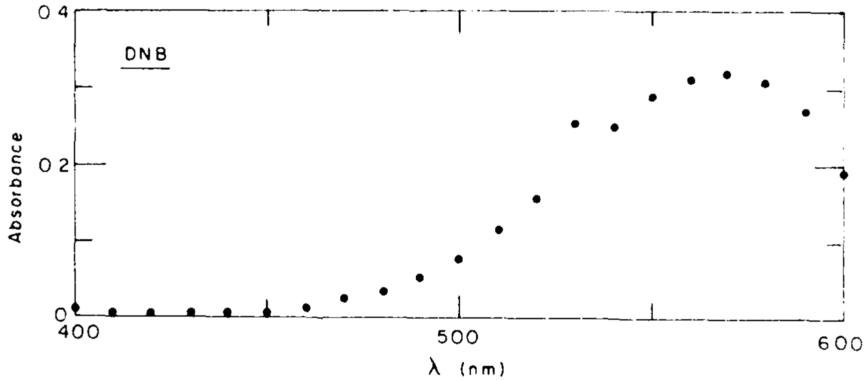


Figure 5. Visible absorbance spectrum of anion from DNB in acetone.

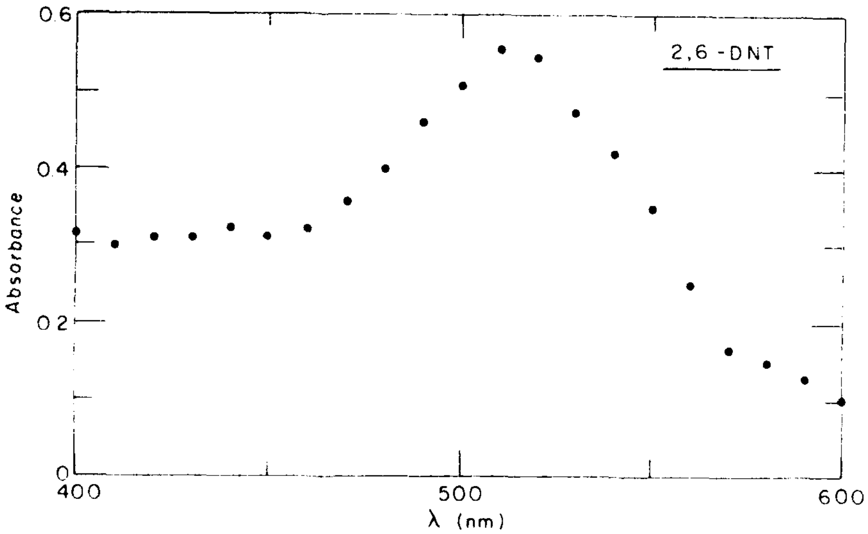


Figure 6. Visible absorbance spectrum of 2,6-DNT in acetone.

Table 3. Effect of various water contents on the absorbance of TNT anions in acetone.

Conc. of water in acetone (% by wt)	*Corresponding* soil moisture content (% of wet wt)*	*Absorbance (540 nm) for 1.9-mg/L TNT solution (A.U.)*
0.0	0.0	0.076
3.0	12.2	0.183
5.9	24.8	0.181
8.9	38.7	0.158
11.7	52.5	0.140
17.4	83.4	0.136
28.2	†	0.054
53.4	†	0.014

* Corresponding soil moisture contents on a wet weight of soil basis if 20 g of soil is extracted with 100 mL of acetone.
† Exceeds possible water present in 20 g of wet soil.

ticle size distribution, recent rainfall events, and proximity to the groundwater table. A test was conducted to assess the effect of variable water concentrations on the absorbance of TNT anions in acetone.

A series of 1.9-mg/L solutions of TNT in acetone were prepared with water contents ranging from 0 to 53% by weight. Jackson–Meisenheimer anions were generated as usual and the absorbance of each solution was obtained at 540 nm (Table 3).

The results indicate that absorbance is dependent on the amount of water present in the acetone. When no water is present, absorbance is low, probably a result of poor solubility of the solid reactants (KOH and Na_2SO_3) in acetone. When relatively large amounts of water are present, the absorbance is also low. At intermediate concentrations of water in acetone (1–17%), however, similar absorbances (±15%) are obtained. If a 20-g sample of wet soil is extracted with a 100 mL of acetone, the 1–17% range of water in acetone would correspond to soil moisture contents ranging from 5–83% (on a wet weight of soil basis). This range of moisture content should include the large majority of surface soils from potentially contaminated sites.

Reagent contact time

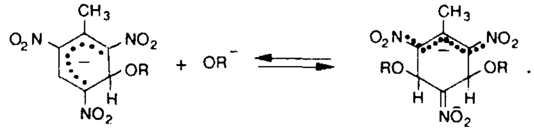
An experiment was conducted to determine if reagent contact time had an effect on the absorbance obtained. A 1.9-mg/L TNT solution was prepared in acetone containing 3.8% water. Six 25-mL aliquots of this solution were placed in individual glass vials and a pellet of KOH and about 0.2 g of Na_2SO_3 were added. The vials were manually shaken for periods ranging from 1 to 4 minutes and two vials had an additional 5 and 15 minutes of reagent contact time. After the chosen contact times, the solutions were filtered as usual and the absorbances measured at 540 nm. All experiments were conducted at laboratory temperatures (22°C ±2°). The results are presented in Table 4.

Table 4. Effect of measured absorbance at 540 nm on reagent contact time for TNT solutions in acetone (3.8% water).

Reagent contact time (min)	*Absorbance (540 nm)*	
	1.9 mg/L of TNT	*7.6 mg/L of TNT*
1	0.198	—
1.5	—	0.379
2	0.198	—
2.5	—	0.76
3	0.196	—
3.5	—	0.76
4	0.193	—
8	0.182	0.76
18	0.157	—

Clearly the reaction takes place rapidly for the 1.9-mg/L solution, with maximum absorbance obtained for the 1- and 2-minute reagent contact times. Absorbances declined for contact times greater than 2 minutes with a 20% reduction by 18 minutes.

To determine if this effect was concentration dependent, a 7.6-mg/L solution of TNT was prepared in acetone (3.8% water). This concentration corresponds to 38 µg/g of TNT in soil using the extraction conditions described. Four aliquots were shaken with KOH and Na_2SO_3, as described above, for periods of 1.5, 2.5, 3.5 and 8 minutes prior to filtering and measuring the absorbance at 540 nm (Table 4). For this solution, the maximum absorbance was obtained for samples with contact times of 2.5 minutes or greater. One interpretation of these results is that the rate limiting step is the dissolution of the solid reactants. For the 1.9-mg/L test solution, sufficient reagent dissolved to completely convert the TNT present to the anion within 1 minute. For the 7.6-mg/L solution, a longer period of 2.5 minutes was required before sufficient reagent had dissolved. If this is the case, the concentration of water in the acetone is also likely to have an effect on the rate of reagent dissolution as well, and the optimum reagent contact time will be difficult to predict for a given extract. The rate of decline of absorbance for excess contact time, however, is relatively slow. The reason for the reduction in absorbance for longer contact times is uncertain but may be due to further reaction of the initial anion produced with a second reactant, as shown in eq 6, with production of a dianion (Terrier 1982):



(6)

Based on these tests, a reagent contact time of three minutes was selected for the following reasons. For

very high TNT concentrations, three minutes may be insufficient to attain the maximum absorbance, but the absorbance will exceed 1.0 A.U. (absorbance unit) for this case and thus the extracts will have to be diluted and reanalyzed anyway. For very low TNT concentrations or solutions with less dissolved water, the measured absorbance will be reduced below its maximum value but the amount of reduction will be very small. For field measurements, the ambient temperature can have an influence on the proper reagent contact time. Observation of the rate of color development for the standard will assist in choosing the most appropriate time for a given temperature.

Stability of filtered solutions

A test was conducted to determine if the colored anions formed from TNT were stable with time after filtration. Filtration removes the colored anions from further contact with the solid reactants. A 1.9-mg/L TNT solution in acetone containing 3.8% water was used. The absorbance at 540 nm was obtained for a variety of time periods after filtration to remove the solid reactants (Table 5).

Table 5. Stability of absorbance for a filtered solution of 1.9-mg/L TNT reacted with KOH and Na_2SO_3.

Time after filtration (min)	*Absorbance (540 nm)*
1	0.197
2	0.197
5	0.196
7	0.196
9	0.197
12	0.197
15	0.197
22	0.198
42	0.198
67	0.205*
120	0.208*

* Higher values due to evaporation of acetone and the resulting concentration of the anion.

The results indicate that filtered solutions are stable for at least two hours and there is no need to take special precautions to make absorbance measurements at a specific time interval following filtration.

Instrument calibration

Spectrophotometric procedures ideally follow the Beer–Lambert law where absorbance is linearly related to concentration:

$$A = abc \tag{7}$$

where A = absorbance
a = absorptivity
b = path length of the cuvette
c = concentration.

Thus, the expected relationship of A vs C is linear through the origin. The following calibration experiment was conducted to determine the concentration range of conformance to the Beer–Lambert law.

A series of TNT standards were prepared in acetone at concentrations ranging from 0.10 to 20.0 mg/L. These standards correspond to soil extracts from soils containing TNT in the range 0.50 to 100.0 µg/g (if 20 g of soil is extracted with 100 mL of acetone).

Two replicate 100-mL aliquots of each standard and blank acetone were placed in individual 250-mL glass bottles and 3.0 mL of water added to each. The water was added to simulate the water that would be extracted

Table 6. Instrument calibration results.

TNT concentration in standard		*Absorbance (540 nm)*	
Solution basis (mg/L)	*Soil basis (µg/g)*	*Replicate 1*	*Replicate 2*
0	0	0.004	0.002
0.10	0.50	0.011	0.014
0.20	1.00	0.021	0.018
0.40	2.00	0.038	0.038
1.00	5.00	0.096	0.093
2.00	10.0	0.183	0.180
4.00	20.0	0.346	0.393
10.0	50.0	0.910	0.890
20.0	100	1.70	1.71

from undried field soils. A 20-mL portion from each bottle was reacted with KOH and sodium sulfite and the absorbance obtained at 540 nm. The results are presented in Table 6.

The linearity of the relationship between concentration and absorbance was assessed using least-squares regression analysis at the 95% confidence level (Table 7). This analysis indicated a significant F ratio of 3.60 for lack of fit (table value = 3.58) when the entire concentration range was used. Inspection of the plot indicated possible curvature at the highest concentration standard. The highest standard was dropped and the regression analysis was repeated. The lack of fit was not significant at the 95% confidence level (F ratio = 0.12 compared to a table value of 3.97) for this reduced con-

Table 7. Results of linear least-squares regression analysis of calibration data.

Concentration range (μg/g)	Absorbance range (AU)	Slope	Intercept	Statistical significance* Lack-of-fit	Zero intercept hypothesis
0.50–100	0–1.71	0.0171	0.0116	Significant	
0.50–50	0–0.91	0.0181	0	Non-significant	Accepted

centration range, indicating that the linear model adequately described the data. The models with and without intercepts were then obtained and a zero intercept test conducted at the 95% confidence level. The *F* ratio was not significant ($F = 0.88$ compared to the table value of 4.75), indicating the intercept was not significant at the 95% confidence level. Thus the zero intercept linear model shown in Table 7 adequately describes the calibration data over the range 0.5 to 50 μg/g, indicating that the Beer–Lambert law applies up to an absorbance of 0.91. Thus for daily calibration, a replicated single point standard should be sufficient.

Absorbance spectra of soil extracts

Since measurements of TNT concentrations in soils will utilize soil extracts, the background absorbance of the acetone extract of soil is important. Although the composition of soils varies widely from location to location, a commercial potting soil was initially selected for study because its very high humus content would produce a worst-case background problem.

A sample of 20 g of moist potting soil was extracted with 100 mL of acetone by shaking in a 250-mL glass bottle for five minutes, allowing the soil to settle for three minutes and filtering the sample through a 0.5-mm Millex SR filter. The absorbance spectrum of the pale yellow filtrate was obtained from 400–600 nm (Fig. 7). A pellet of KOH and about 0.2 g of Na_2SO_3 were then added to the filtrate in a cuvette and the bottle was shaken for 5 minutes. The solution was filtered through a fresh Millex SR filter into a clean cuvette and the spectrum again obtained from 400–600 nm (Fig. 7).

The initial absorbance of the soil extract was considerably greater between 400–500 nm than between 500–600 nm. After the extract was allowed to react with KOH and Na_2SO_3, the absorbance approximately doubled over the entire range of wavelengths, with rather large absorbances toward 400 nm.

The results of this test indicate that a blank absorbance measurement must be made on acetone soil extracts prior to addition of KOH and Na_2SO_3 to account for background absorbance of humic materials that could be present in the extracts. For the extract from the potting soil the intensity of this background absorbance increases substantially after addition of KOH and Na_2SO_3 even when TNT is absent. To determine if the factor of two increase in absorbance for the potting soil extract is typical of extracts from other soils, a series of blank soils from eight different military sites and a sample of USATHAMA Standard Soil were extracted with acetone and the absorbance at 540 nm obtained on the filtered extracts before and after addition of KOH and Na_2SO_3. The ratio of the absorbance after reagent addition to that before reagent addition ranged from 1.1 to 3.5 with a mean value of 2.1 (Table 8). Thus, to correct for background absorbance, the initial blank reading should be doubled and subtracted from the absorbance reading obtained after addition of the reagents. In addition a wavelength of 540 nm should be used to estimate TNT concentration. While the molar absorptivity for the TNT anions is greater at 462 nm, the

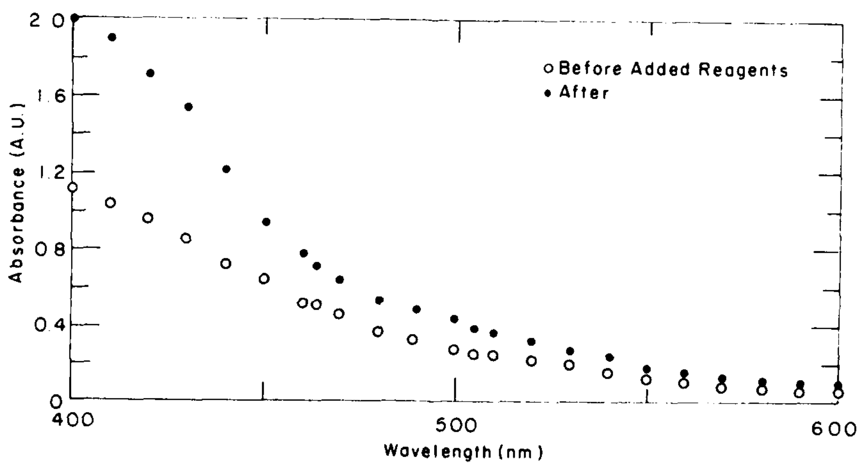


Figure 7. Visible absorbance spectrum of acetone extract of high humus potting soil, before and after addition of KOH and Na_2SO_3.

contribution from the blank in this spectral region is considerably higher than at 540 nm and would thus lead to a greater uncertainty in calculated concentrations.

Table 8. Absorbance measurements for acetone extracts of blank soils, before and after addition of KOH and Na_2SO_3.

Sample location	*Absorbance (540 nm)* Before	After	Ratio After/Before
USATHAMA Std. Soil	0.002	0.007	3.5
Keystone Ordnance Works (Pa.)	0.001	0.003	3.0
Lake Ontario Ordnance Works (N.Y.)	0.003	0.005	1.7
Susquehana Ordnance Depot (Pa.)	0.003	0.004	1.3
Raritan Arsenal (N.J.)	0.005	0.015	3.0
Hawthorne Army Amunition Plant (Nev.)	0.000	0.002	—
Hastings East Industrial Park (Neb.)	0.019	0.030	1.6
Fort Hancock (N.J.)	0.005	0.006	1.2
Weldon Springs Training Area (Mo.)	0.123	0.140	1.1
			$\bar{x} = 2.1$

Extraction efficiency of field procedure

For a field method to provide accurate estimates of TNT concentration in the soil, the extraction step must be rapid. Previous extraction studies have indicated that rather long extraction times were required to achieve good recovery when acetonitrile or methanol were used as the extraction solvent (Jenkins and Grant 1987). No results were available for acetone, however.

In order to determine how rapidly acetone will extract TNT from soil, 16 field-contaminated soil samples from nine different sites were extracted with acetone as follows. Approximately 20 g of each air-dried soil was placed in 250- mL glass bottles and 3.0 mL of water added to each. Water was added to simulate a field soil that would have moisture present under normal conditions. A 100-mL aliquot of acetone was added to each bottle, the bottles were shaken by hand for three minutes and then the soil was allowed to settle for 5 minutes. A 50-mL aliquot of each extract was then removed and analyzed by RP-HPLC (Jenkins et al. 1989). Concentrations of TNT in these extracts correspond to the concentrations that would be present when the method was used under field conditions (Table 9).

The remaining soil/acetone slurries were shaken to resuspend the soil and placed in an ultrasonic bath for 18 hours. The bath was maintained at less than 32°C during this period. After sonication, the soil was allowed to settle for an hour and an aliquot of each extract removed. The mass of TNT in this 50-mL extract was determined and added to that removed with the first 50-mL aliquot. The concentration was then calculated based on the weight of soil used. These values are shown in Table 9 under the heading of "Laboratory Extraction Procedure."

Table 9. Comparison of extraction efficiency for field procedure vs standard laboratory method.

Sample origin	*TNT concentration (µg/g)* Field extraction procedure* (µg/g)	Laboratory extraction procedure†	Recovery by field method**
Vigo Chemical Plant (Ind.)	11.7	13.4	87.3%
Hawthorne AAP (Nev.)-A	4.53	4.75	95.4%
Nebraska Ordnance Works (Neb.)-A	0.065	0.071	91.5%
Nebraska Ordnance Works (Neb.)-B	340	349	97.4%
Hastings East Indus. Park (Neb.)	67.6	68.8	98.3%
Weldon Springs Training Area (Mo.)-A	0.96	1.26	76.2%
Sangamon Ordnance Plant (Ill.)	21.5	23.2	92.8%
Weldon Springs Training Area (Mo.)-B	163	176	92.6%
Hawthorne AAP (Nev.)-B	5.79	5.65	102.5%
Nebraska Ordnance Works (Neb.)-C	63.5	67.9	93.5%
Raritan Arsenal (N.J.)	71.7	80.6	89.0%
Nebraska Ordnance Works (Neb.)-D	0.39	0.32	121.9%
Lexington-Bluegrass Depot (Ky.)	5.90	7.11	83.0%
Chickasaw Ordnance Works (Tenn.)	0.21	0.16	131.3%
Hawthorne AAP (Nev.)-C	0.79	0.90	87.8%
Weldon Springs Training Area (Mo.)-C	0.075	0.077	97.4%
			$\bar{x} = 96.1$
			$s = 13.6$

* 20 g soil shaken with acetone for 3 minutes.

† 20 g soil extracted with acetone for 18 hours in sonic bath.

** Relative to laboratory procedure.

For 13 of the 16 samples, the 18-hour extraction resulted in higher estimates of soil TNT concentration than did the 3-minute field procedure. For the other three soils a small decrease was found in TNT concentration after 18-hour sonication. The average recovery after the 3-minute extraction period ranged from 76 to 131% with a mean of 96% of that at 18 hours, indicating that acetone is an excellent extraction solvent with respect to its extraction kinetics. Acetone is not used in the standard RP-HPLC laboratory procedure (Jenkins et al. 1989) since it absorbs in the ultraviolet, thereby interfering with the determination of HMX and RDX. In addition, several analytes including TNB are not stable in acetone. For the field method using rapid colorimetric analysis, however, these limitations do not apply. The results indicate that recoveries are very good from concentrations as low as 0.071 µg/g to as high as 349 µg/g. Thus, the accuracy of the field method is not limited by slow extraction kinetics and a 3-minute period of manual shaking is sufficient.

Comparison of TNT concentration estimates for soil extracts

The extracts obtained after manually shaking the soil with acetone, described above, were also analyzed by a colorimetric procedure utilizing the Jackson–Meisenheimer anions. To do so, the initial absorbance of the filtered extracts was obtained at 540 nm. A 20-mL sample of the extract was placed in a scintillation vial, KOH and sodium sulfite were added and the vials were shaken manually for 3 minutes. The vials were allowed to stand for 5 minutes and the solution filtered into a clean cuvette. The initial absorbance, before the reagents were added, was doubled and subtracted from the absorbance obtained after reagent addition; the resulting difference was used to estimate TNT concentration. TNT estimates for the 16 field-contaminated soils are given in Table 10. For comparison, the results of analysis of the extracts for TNT by the standard RP-HPLC procedure (Jenkins et al. 1989) are also presented along with the estimates of TNB concentration obtained from a separate subsample extracted with acetonitrile. TNB could not be reliably determined in these extracts due to its instability in acetone.

The colorimetric results were correlated against both the TNT estimate by HPLC and the sum of TNT and TNB. The correlation with TNT alone resulted in a slope of 0.59 and an R^2 of 0.943 (Fig. 8). The correlation with TNT plus TNB resulted in a slope of 0.86 and an R^2 of 0.985 (Fig. 9). A paired t test indicated that the concentration estimates for TNT from the colorimetric method and the sum of TNT and TNB by the HPLC procedure were not significantly different at any level of significance. Thus it appears that the colorimetric results are best represented as the sum of TNT plus TNB. As discussed earlier, the γ_{max} for TNT and TNB are quite similar with nearly equivalent molar absorptivities. The slope of 0.86 indicates that, in general, the colorimetric procedure gives a slightly greater estimate for TNT than can be accounted for by TNT and TNB.

Table 10. Comparison of colorimetric and RP-HPLC analysis of soil extracts.

Sample origin	*TNT concentration* Colorimetric method (µg/g)	RP-HPLC method (µg/g)	*TNB concentration** RP-HPLC method (µg/g)
Vigo Chemical Plant (Ind.)	13.5	11.7	<d
Hawthorne AAP (Nev.) - A	5.49	4.53	<d
Nebraska Ordnance Works (Neb.) - A	2.39	0.065	2.72
Nebraska Ordnance Works (Neb. - B	592	340	157
Hastings East Indus. Park (Neb.)	85.3	67.6	2.7
Weldon Springs Training Area (Mo.) - A	4.02	0.96	0.3
Sangamon Ordnance Plant (Ill.)	32.7	21.5	0.68
Weldon Springs Training Area (Mo.) - B	145	163	19.3
Hawthorne AAP (Nev.) - B	8.67	5.79	3.2
Nebraska Ordnance Works - C	146	63.5	74.1
Raritan Arsenal (N.J.)	85.3	71.7	<d
Nebraska Ordnance Works (Neb.) - D	0.38	0.39	<d
Lexington-Bluegrass Depot (Ky.)	15.0	5.90	<d
Chickasaw Ordnance Works (Tenn.)	<d	0.21	<d
Hawthorne AAP (Nev.) - C	1.20	0.79	<d
Weldon Springs Training Area (Mo.) - C	0.33	0.075	<d

* Obtained from a separate subsample using acetonitrile extraction, as described in Jenkins et al. (1989).

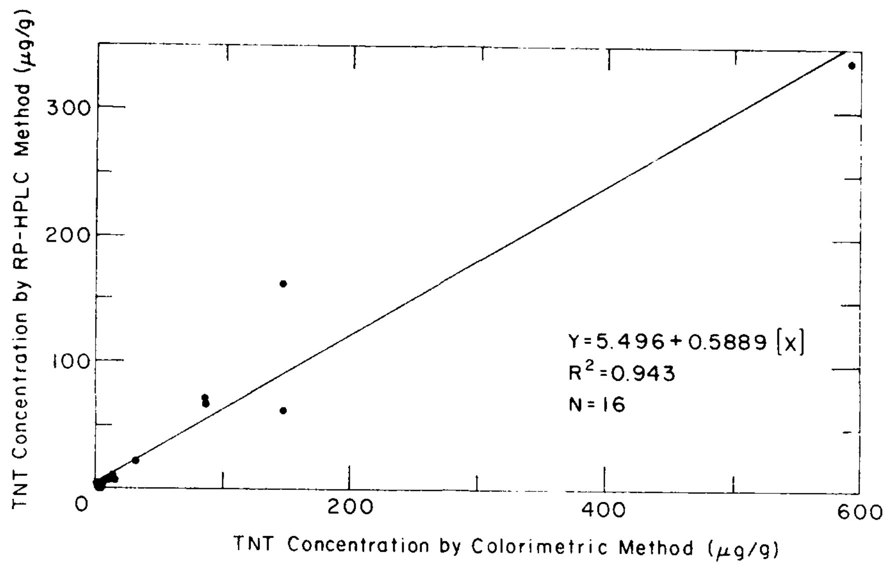


Figure 8. Correlation of TNT concentration estimate from colorimetric procedure vs RP-HPLC method using field-contaminated soils.

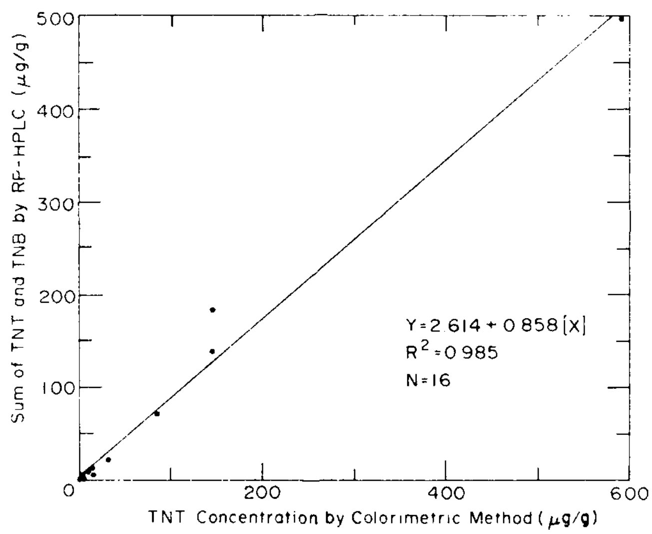


Figure 9. Correlation of concentration estimate using colorimetric method for TNT vs the sum of TNT and TNB from RP-HPLC analyses.

One interpretation of these results is that other TNT degradation products such as trinitrobenzoic acid, trinitrobenzyl alcohol, and trinitrobenzaldehyde (Walsh 1990), which are not identifiable by RP-HPLC analysis of the extracts, form colored Jackson–Meisenheimer anions.

Certification testing

Since results with field-contaminated soils appeared very encouraging, we subjected the method to the full USATHAMA certification procedure (USATHAMA 1987). To do so, a set of six 20-g subsamples of USATHAMA standard soil were moistened with 3 mL of water and spiked with concentrations of TNT corresponding to soil concentrations ranging from 0 to 22.25 µg/g on each of four days (App. A). The spiked soils were allowed to stand for 1 hour and the TNT extracted with 100 mL of acetone by manually shaking for 3 minutes. The soil was then allowed to settle for 5 minutes and a 25-mL aliquot of the extract filtered through a 0.5 mm Millex-SR disposable filter unit into a clean cuvette. The background absorbance was then obtained at 540 nm prior to the addition of one pellet of KOH and about 0.2 g of Na_2SO_3. The cuvette was capped,

Table 11. Results of certification testing.

Spiked TNT concentration (µg/g)	Found TNT concentration (µg/g)			
	Day 1	Day 2	Day 3	Day 4
0	0.14	0.32	0.25	0.24
1.11	1.11	1.30	1.34	1.29
2.23	1.98	2.61	2.36	2.37
4.45	4.75	4.96	4.58	4.34
11.1	10.6	11.1	11.5	11.9
22.3	23.5	22.9	22.8	22.3

shaken for 3 minutes and the solution filtered into a clean cuvette. The absorbance was then obtained again at 540 nm. The background absorbance was doubled and subtracted from the final absorbance, and the difference was used to estimate TNT concentrations (Table 11).

Regression analysis of the results of the found vs spiked concentration was obtained using linear models with and without an intercept. The lack-of-fit ratio was nonsignificant at the 95% confidence level in both cases, indicating that results were satisfactorily described by a linear relationship (App. A). A zero intercept hypothesis was examined at the 95% confidence level and the results indicated that the intercept was nonsignificant. Thus the slope of the zero intercept, linear model can be usedas an estimate of analyte recovery. A slope of 1.026 was obtained from regression analysis, indicating recovery was essentially quantitative.

The certified reporting limited (CRL) was obtained using the method of Hubaux and Vos (1970) as described in USATHAMA (1987) (App. A). The calculated CRL was 0.72 µg/g. Since the lowest tested standard was 1.11 µg/g, this higher value is considered the CRL according to the USATHAMA policy. A lower CRL would be obtained, however, if lower spike levels were included in the test (Grant et al. 1989).

Field testing

The method was given a field test at Umatilla Army Depot, Umatilla, Oregon. A number of soil/sediment samples were collected from the top 2 ft (65 cm) of a dry disposal lagoon. The samples were collected in glass bottles and transported to a nearby office building where analysis was conducted.

Since TNT concentrations were expected to be very high, a 2-g subsample of each soil (rather than the normal 20-g samples) was placed to a small plastic bottle and 50 mL of acetone was added. The bottles were shaken a minimum of 3 minutes and allowed to settle at least 15 minutes. A 25-mL aliquot was then filtered through a Millex SR filter into a clean cuvette. An aliquot of each extract (the volume depended on the color of the acetone extract) was then removed with a glass pipet and placed in a 100-mL graduated cylinder. A volume of 3 mL of water was added and the total volume diluted to 100 mL with acetone. The background absorbance of this solution was obtained at 540 nm using the Hach spectrophotometer. A 25-mL aliquot was reacted with KOH and sodium sulfite, the cuvette was capped, shaken for 5 minutes and allowed to stand another 5 minutes.* The liquid was then filtered through a Millex SR filter into a clean cuvette and the absorbance measured at 540 nm.

The background absorbance was doubled and subtracted from the final absorbance and the TNT concentration estimated from the difference (Table 12).

Table 12. Comparison of results of field samples from Umatilla Depot using field and laboratory methods.

Sample	TNT concentration (µg/g)*	
	Field method	RP-HPLC lab method
1b	1060	2250
2a	3560	7430
3b	704	1180
3a	3180	4030
4a	4490	8520
5a	2530	3990
6a	84	131
8a	102000†	38600†
9a	6610	7690
11a	716	1300
12a	109	183

* Both laboratory and field method results are reported on a dry weight of soil basis to enable direct comparison.

† Results for this sample were very different than observed for others and, because of very high values, the results were not included in correlation analysis.

The remainder of each soil–sediment sample was returned to CRREL and analyzed for TNT using the standard laboratory procedure (Jenkins et al. 1989). The results are included in Table 12 for comparison.

Except for sample 8a, the results of laboratory analysis are higher than those obtained using the field method. Correlation analysis of the field and laboratory results was conducted. Sample 8a was not included in the correlation analysis because very different behavior was observed for this sample and the TNT concentration was an order of magnitude higher than for any of the other samples. The correlation for the remaining 10 samples was excellent with an R^2 value of 0.865, which

* The test was conducted before the importance of reagent contact time was understood.

was significant at the 99% confidence level. The slope of the best fit relationship was 0.627, indicating that the field procedure, on the average, gave results only about 63% as high as the laboratory results. There may be two factors that contributed to the low results for the field method. First, an excessively long reagent contact time prior to filtration was used. Thus the absorbance would have been reduced relative to its maximum value. Second, the TNT concentrations in the Umatilla soil were much higher than in other field-contaminated soils tested and the percentage extracted in the short extraction time used by the field method could be reduced in comparison to the 18-hour extraction used in the laboratory procedure. Nevertheless, the field results were encouraging for a first test.

SUMMARY AND CONCLUSIONS

A simple colorimetric method was developed for the field determination of TNT in soil. The procedure involves extraction of the soil with acetone followed by use of the Janovsky reaction, where nitroaromatic compounds in acetone form characteristically colored solutions in the presence of strong base. A detailed description of the method in USATHAMA format is provided in Appendix A.

For this field method, soils are extracted by manually shaking a 20-g portion of soil with 100 mL of acetone for 3 minutes. Acetone extracts are filtered through a Millex SR disposable filter assembly and the initial absorbance is obtained at 540 nm. One pellet of KOH and about 0.1 to 0.5 g of Na_2SO_3 is added and the extracts manually shaken for 3 minutes. The solutions are immediately filtered through another Millex SR filter and the absorbance at 540 nm measured again. Absorbance was found to follow the Beer–Lambert law through the absorbance of 0.91 A.U.

Comparison of TNT concentrations in the extract with the more exhaustive laboratory extraction procedure indicated that good recovery was achieved for moderately contaminated soils. This is probably due to the very high solubility of TNT in acetone (109 g/100 mL at 20°C). Poorer recovery, averaging about 63%, was found for the very highly contaminated soils encountered in the field test.

Experiments with a series of uncontaminated (blank) soils indicated that acetone also extracts variable amounts of yellowish material from soil, but these substances absorb only weakly at 540 nm. Treatment of these yellowish extracts with KOH and Na_2SO_3 resulted in an approximate doubling of the absorbance at 540 nm. This increased absorbance must be included in blank corrections.

Estimates of TNT concentration in a number of field-contaminated soils were obtained using this colorimetric approach and compared with results from the standard laboratory procedure. An excellent linear correlation was obtained when the TNB concentration was added to the TNT results for the laboratory method. Thus the colorimetric procedure actually measures the sum of TNT and TNB.

The method was tested using the 4-day USATHAMA certification procedure (App. A). A certified reporting limit of 1.1 µg/g was obtained. A linear relationship was found between spiked and determined concentration over the range of 1.1 to 22.2 µg/g. Extracts from soils with higher concentrations should be diluted with acetone prior to addition of the reagents such that the corresponding absorbance is below 0.7 A.U.

The procedure was field tested at Umatilla Army Depot. Concentration estimates for TNT in soils from an old disposal lagoon correlated well with results obtained using the standard laboratory procedure.

The procedure described in this report was designed for determining TNT in soil. This approach could also be configured to determine TNT in water if a preconcentration step was included.

LITERATURE CITED

Baernstein, H.D. (1943) Photometric determinations of benzene, toluene and their nitro derivatives. *Industrial and Engineering Chemistry, Analytical Edition*, **15**: 251–253.

Bost, R.W. and F. Nicholson (1935) A color test for the identification of mono-, di-, and trinitro compounds. *Industrial and Engineering Chemistry, Analytical Edition*, **7**: 180–191.

Erickson, E.D., D.J. Knight, D.J. Burdick and S.R. Greni (1984) Indicator tubes for the detection of explosives. Naval Weapon Center Report NWC TP-6569, China Lake, California.

Grant, C.L., A.D. Hewitt and T.F Jenkins (1989) Comparisons of low concentration measurement capability estimates in trace analysis. Method detection limit and certified reporting limit. USA Cold Regions Research and Engineering Laboratory, Special Report 89-20.

Hall, T.N. and C.F. Poranski, Jr. (1970) Chapter 6: Polynitroaromatic addition compounds. In *The Chemistry of the Nitro and Nitroso Groups* (H. Feuer, Ed.). New York: Interscience Publishers.

Heller, C.A., S.R. Greni and E.D. Erickson (1982) Field detection of 2,4,6-trinitrotoluene in water by ion-exchange resins. *Analytical Chemistry*, **54**: 286–289.

Hubaux, A. and G. Vos (1970) Decision and detection limits for linear calibration curves. *Analytical Chemistry*, **42**: 840–855.

Jackson, C.L. and R.B. Earle (1903) On certain colored substances derived from nitro compounds. *American Chemical Journal*, **29**: 89–120.

Janovsky, J.V. (1891) Uber eine Reaction der Dinitrokörper. *Berichte*, **24**: 971–972.

Jenkins, T.F. and C.L. Grant (1987) Comparison of extraction kinetics for munitions residues in soil. *Analytical Chemistry*, **59**: 1326–1331.

Jenkins, T.F., M.E. Walsh, P.W. Schumacher, P.H. Miyares, C.F. Bauer and C.L. Grant (1989) Liquid chromatographic method for the determination of extractable nitroaromatic and nitramine residues in soil. *Journal Association of Offical Analytical Chemists*, **72**: 890–899.

Jenkins, T.F. and P.W. Schumacher (1990) Evaluation of a field kit for detection of TNT in water and soil. USA Cold Regions Research and Engineering Laboratory, Special Report 90-20.

Kay, K. (1941) Determination of TNT (2,4,6-trinitrotoluene) in air. *Canadian Journal of Research*, **19**: 86–89.

Meisenheimer, J. von (1902) Uber Reactionen Aromatischer Nitrokörper. *Liebig's Annalen der Chemie*, **323**: 205–246.

Rosenblatt, D.H. (1986) Contaminated soil clean up objectives for Cornhusker Army Ammunition Plant. USA Medical Bioengineering Research and Development Laboratory Technical Report 8603, Fort Detrick, Frederick, Maryland.

Ruchhoft, C.C. and W.G. Meckler (1945) Colored TNT derivative and alpha-TNT vs colored aqueous alpha-TNT solutions, Spectrophotometric procedure for quantitative estimation. *Industrial and Engineering Chemistry, Analytical Edition*, **17**: 430–434.

Taylor, C.A. and W.H. Rinkenbach (1923) The solubility of trinitrotoluene in organic solvents. *Journal of the American Chemical Society*, **45**: 44–59.

Terrier, F. (1982) Rate and equilibrium studies in Jackson–Meisenheimer complexes. *Chemical Reviews*, **82**: 77–152.

USATHAMA (1987) USATHAMA QA program. USA Toxic and Hazardous Materials Agency, Aberdeen Proving Ground, Maryland, 2nd Ed.

U.S. Army (1984) Military Explosives, TM 9-1300-214. Headquarters, Department of the Army (September 1984).

Walsh, M.E. (1990) Environmental transformation products of nitroaromatics and nitramines. Literature review and recommendations for analytical method development. USA Cold Regions Research and Engineering Laboratory Special Report 90-2.

Yinon, J. and S. Zitrin (1981) *The Analysis of Explosives*. Oxford: Pergamon Press.

APPENDIX A: METHOD DOCUMENTATION (USATHAMA 1987) FORMAT CERTIFICATION FIELD METHOD FOR THE DETERMINATION OF 246 TNT IN SOIL

I. Summary

A. Analytes: This method is suitable for determining the concentration of 246 TNT in the field using battery-operated equipment.

B. Matrix: This method is suitable for the determination of 246 TNT in soil or sediment.

C. General Method: A 20-g subsample of undried soil is placed in a 4-oz (120-mL) glass bottle and 100 mL of acetone added. The bottle is capped and shaken manually for three minutes. The bottle is then allowed to stand for 5 minutes to allow the particles to settle, and then a 25-mL aliquot of the extract is filtered through a 0.5-mm Millex SR filter into a 25-mL cuvette. The absorbance of this solution is obtained at 540 nm. About 0.1 to 0.5 g of sodium sulfite (Na_2SO_3) and one pellet of potassium hydroxide (KOH) are added, the cuvette capped and shaken for 3 minutes. The resulting solution is immediately poured into the barrel of a 50-mL plastic syringe and filtered through another Millex SR filter into a clean cuvette. The absorbance is again measured at 540 nm as soon as possible (within 60 minutes) after filtration. The initial absorbance difference is doubled and subtracted from the final reading and this is proportional to 246 TNT concentration.

II. Application

A. Calibration Range:

The calibrated range over which measurement can be made is 1.11 to 22.3 µg/g. Concentrations in excess of 22.3 µg/g can be obtained by volumetric dilution of the extract with acetone such that the measured absorbance is less than 0.6 absorbance units. Whenever dilutions are made, a small amount of water is added (3 mL to 100 mL of solution) to ensure that sufficient solubility of the reagents is maintained. When this is done, the background absorbance is obtained after the addition of water.

B. Tested Concentration Range: This method was tested over the range of 246 TNT concentration from 1.11 to 22.3 µg/g.

C. Sensitivity: The absorbance per µg/g of 246 TNT was found to be 0.029 absorbance units, resulting in 0.032 absorbance units at the certified reporting limit (1.11 µg/g).

D. Interferences: A number of other nitroaromatic compounds were found to develop a visible color as well as 246 TNT. The colors observed are given below:

Tetryl—Orange
TNB—Red
DNB—Purple
2,4-DNT—Blue
2,6-DNT—Pink

No color development was observed for: RDX, HMX, Nitrobenzene, o-nitrotoluene, m-nitrotoluene, p-nitrotoluene, nitroglycerine, 4-amino-2,6-dinitrotoluene or 2-amino-4,6-dinitrotoluene. Humic organic matter, normally present in soil, is extracted to some degree and will result in a yellow extract that becomes darker yellow on addition of the reagents. The contribution to the absorbance at 540 nm is small but can be corrected by doubling the absorbance reading before addition of reagents and subtracting from the absorbance after addition of KOH and Na_2SO_3.

E. Safety Information: The normal safety precautions associated with the use of a flammable organic solvent should be employed. If acetone containing KOH is spilled on the skin, it should be rapidly rinsed off with water. Eye protection is recommended when shaking bottles or cuvettes to protect against splash from poorly sealed containers.

III. Apparatus and Chemicals

A. Instrumentation

1. Field portable, battery-operated colorimeter (HACH DR2 spectrophotometer or equivalent, bandpass 20 nm).
2. Mechanical balance, to measure soil weights.

B. Analyte

246 TNT (2,4,6-trinitrotoluene)
BP: 280°C (explodes)
MP: 80.1°C
Solubility in water: 130 mg/L
Octanol/water partition coefficient: 68
CAS # 118-96-7.

C. Reagents and SARMs:

1. 246 TNT (SARM quality)
2. Acetone
3. Potassium hydroxide, reagent grade pellets
4. Sodium sulfite, reagent grade.

D. Glassware/Equipment

1. 4 oz (Qorpak or equivalent) glass bottles with caps
2. Glass volumetric pipets
   - 0.50 mL
   - 1.00 mL
   - 2.00 mL
   - 5.00 mL
   - 10.00 mL
   - 25.0 mL
3. 100-mL graduated cylinder
4. Cuvette bottles with caps (25-mL capacity), 25-mm path length.
5. Glass volumetric flask (2)—50 mL.
6. Filters (Millex SR, 0.5 µm)
7. Syringes (Plastipak), 20 and 50 mL.
8. Forceps.
9. Spatula.

IV. Calibration

A. Initial Calibration:

1. Preparation of Standards

Solid TNT (SARM or reagent grade) was dried to constant weight in a vacuum desiccator in the dark. About 0.1 g is weighed out to the nearest 0.1 mg, transferred to a 250-mL volumetric flask and diluted to volume with acetone. The TNT concentration of this stock standard is about 400 mg/L. This stock standard should be prepared in the laboratory before going to the field.

A working stock standard is prepared by diluting 25.0 mL of the stock TNT standard to 250 mL in a glass volumetric flask and bringing to volume with acetone. The concentration of this working stock standard is about 40 mg/L.

Calibration solutions are prepared as described in Table A1. Glass volumetric pipettes are used to dispense the working stock standard and the distilled water, and a 100-mL graduated cylinder is used to add the acetone. Each solution is prepared in a 4-oz glass bottle, capped and shaken.

2. Instrument Calibration

Approximately 0.2 g of sodium sulfite (excess) and one pellet of potassium hydroxide are added to a 25-mL aliquot of each standard; samples are shaken for 3 minutes and allowed to stand 2 minutes. The solutions are then filtered into a 25-mL glass cuvette bottle (19-mm path length) and the absorbance measured at 540 nm using a battery-operated spectrophotometer. The zero absorbance setting was first established using pure acetone, and the instrument was zeroed according to manufacture's instructions.

Table A1. Preparation of calibration solutions.

Solution	Volume of working std. (mL)	Volume of acetone added (mL)	Volume of distilled water added (mL)	Approx.* conc. (mg/L)	As iated† soil conc. (µg/g)
A	0	100	3.00	0.0	0.0
B	0.50	99.5	3.00	0.2	1.0
C	1.00	99	3.00	0.4	2.0
D	2.00	98	3.00	0.8	4.0
E	5.00	95	3.00	2.0	10.0
F	10.00	90	3.00	4.0	20.0

* Does not include volume of water. The reason is that all field soils will contain water of an unknown quantity and all calculations will ignore this small volume contribution.
† This concentration is the comparable soil RDX concentration if 20 g of soil is used and 100 mL of acetone used for extraction. The concentration is based on wet weight of soil.

3. Calculations

Absorbance readings for solutions A-F should be in a range from 0.0 to 0.7 absorbance units. If so, the absorbance should be linear with TNT concentration on either a milligram per liter basis or an equivalent microgram per gram of wet soil basis. The slope of this relationship (or the response factor) was found to average about 0.15 absorbance units per mg/L in the extract (or about 0.029 absorbance units per µg/g of wet soil).

B. Daily Calibration

Since a linear relationship with zero intercept is the expected result for initial calibration, daily calibration is obtained using solution E (Table A1) and calculating a response factor as described above.

V. Certification Testing

A. Preparation of Spiking Solutions:

The spiking stock standard is prepared in an identical manner to the calibration stock standard described in Section IV-A-1. The soil spiking solution is prepared in an identical manner to the working stock standard also described in Section IV-A-1.

B. Soil Spiking

Subsamples of 20.0 g of USATHAMA Standard Soil are placed in each of six 4-oz glass bottles. A 3.00-mL aliquot of water is added to each since the standard soil has been previously dried. The six bottles are labeled, blank, 0.5X, 1X, 2X, 5X and 10X. Aliquots of the TNT spiking solution are added to these bottles as described in Table A2. The spiked soils are allowed to stand for 1 hour capped prior to extraction.

Table A2. Preparation of spiked soils.

Designation	Volume of TNT Spiking solution added (mL)	TNT concentration* (µg/g)
Blank	—	0.0
0.5 X	0.50	.0
1 X	1.00	2.0
2 X	2.00	4.0
5 X	5.00	10.0
10 X	10.00	20.0

C. Soil Extraction and Analysis

A volume of acetone is added to each bottle in a manner to make the total solution volume added (spike + acetone addition) equal 100 mL. The bottles are capped and shaken vigorously by hand for 3 minutes. The soil is allowed to settle for 5 minutes and a 25-mL aliquot filtered through a 0.5-µm Millex SR syringe filter into a 25-mL glass cuvette using a 50-mL Plastipak syringe. The absorbance of this solution is measured on the portable spectrophotometer at 540 nm relative to pure acetone. The cuvette is removed from the instrument, about 0.1–0.5 g of Na_2SO_3 added along with one pellet of potassium hydroxide, and the bottle is capped and manually shaken for 3 minutes. The solution is immediately poured into the barrel of a 50-mL Plastipak syringe equipped with a Millex SR filter. The plunger is replaced and the solution filtered into a fresh 25-mL glass cuvette. The absorbance is again read at 540 nm. The glass cuvette bottles must be thoroughly rinsed with water and acetone between samples.

D. Calculations

The absorbance of the soil extract at 540 nm prior to the addition of the reagents is doubled and subtracted from the absorbance of the extract after addition of the reagents:

TNT absorbance = (Absorbance after) –2 (Absorbance before).

The doubling of the absorbance before the reagents are added takes into account an increase in absorbance due to the reaction of KOH with extracted soil humic materials.

The soil concentration is then obtained by dividing the TNT absorbance by the response factor obtained by analysis of solution E:

$$\text{Soil conc. } (\mu g/g) = \frac{\text{TNT absorbance (absorbance units)}}{\text{Response factor (absorbance units}/\mu g/g)}.$$

VI. Sampling Handling

This method is designed to be used with field soils that have not been previously dried. If dried soils are used, 3.0 mL of distilled water should be added to the 20-g soil sample before extraction.

The soil sample is mixed as thoroughly as possible, a 20-g subsample added to a 4-oz glass bottle and the bottle capped until extraction is conducted. The samples should be kept cold (4°C) and in the dark until extraction takes place. Samples should be analyzed the same day they are collected.

VII. Procedure

A. Sample Processing

A 20-g subsample of soil is added to a 4-oz glass bottle and 100 mL of acetone are added using a graduated cylinder. The bottles are capped and shaken manually for 3 minutes. The soil is allowed to settle for 5 minutes and a 25-mL aliquot is filtered into a 25-mL glass cuvette bottle through a Millex SR syringe filter using a 20-mL Plastipak syringe. The absorbance is obtained at 540 nm relative to pure acetone.

About 0.1–0.5 g of Na_2SO_3 and one pellet of KOH is then added to the cuvette bottle; the bottle capped tightly and shaken manually for 3 minutes to allow full color development. The solution is poured into the barrel of a 50-mL Plastipak syringe which is equipped with a Millex SR filter and filtered into a fresh 25-mL glass cuvette bottle. The absorbance is again obtained at 540 nm. The glass cuvettes must be thoroughly rinsed with water and acetone between samples. If the measured absorbance is greater than 0.7 A.U., an aliquot of the unreacted extract should be diluted with acetone to achieve an absorbance between 0.1 and 0.7 A.U. when reacted with KOH and Na_2SO_3. When dilutions are made, a small volume of water (about 3 mL to a total volume of 100 mL) should be added to ensure that sufficient reagent solubility is maintained.

VIII. Calculations

The TNT absorbance is obtained by subtracting twice the absorbance at 540 nm prior to addition of the reagents from the absorbance after addition of the reagents and dividing by the response factor obtained from analysis of solution E (Table A1) as described in Section V-D.

IX. Daily Quality Control

A blank and a spiked soil at 1X (2 µg/g) are analyzed each day. Results are maintained on a control chart and control limits are established as described in the USATHAMA Installation Restoration Quality Assurance Program.

X. Reference

Jenkins, T.F. (1990) Development of a simplified field method for the determination of TNT in soil. USA Cold Regions Research and Engineering Laboratory, Special Report. (in prep).

U.S. GOVERNMENT PRINTING OFFICE 1990/500-063/22048

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	November 1990	

4. TITLE AND SUBTITLE

Development of a Simplified Field Method for the Determination of TNT in Soil

5. FUNDING NUMBERS

6. AUTHORS

Thomas F. Jenkins

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

U.S. Army Cold Regions Research and Engineering Laboratory
72 Lyme Road
Hanover, New Hampshire 03755-1290

8. PERFORMING ORGANIZATION REPORT NUMBER

Special Report 90-38

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

U.S. Army Toxic and Hazardous Materials Agency
Aberdeen Proving Ground
Maryland 21010

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

CETHA-TS-CR-90125

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

Available from NTIS, Springfield, Virginia 22161.

12b. DISTRIBUTION CODE

13. ABSTRACT (*Maximum 200 words*)

A simple field method was developed for determining the concentration of 2,4,6-trinitrotoluene (TNT) in soil. The method involves extraction of the soil with acetone, generation of the red-colored Jackson–Meisenheimer anion by addition of potassium hydroxide and sodium sulfite, and measurement of color intensity at 540 nm using a battery-operated spectrophotometer. The method was shown to follow the Beer–Lambert law with linear calibration through an absorbance of 0.9 absorbance units, and was found to be both precise and accurate in tests with spiked soils, providing a detection limit of about 1 µg/g. The extraction step recovered a mean of 96% of the TNT recoverable by a more exhaustive laboratory extraction procedure. A comparison was made of concentration estimates from the field method with those from the standard RP-HPLC laboratory procedure using a set of field-contaminated soils. An excellent correlation existed between the two when both 1,3,5-trinitrobenzene and TNT concentrations from the laboratory measurements were included. The method is susceptible to interference from a number of polynitroaromatic compounds including the following: 1,3,5-trinitrobenzene (red), tetryl (orange), 2,6-dinitrotoluene (pinkish purple), 2,4-dinitrotoluene (blue) and 1,3-dinitrobenzene (purple). No color was observed for nitramine explosives, such as RDX or HMX, or nitrate esters such as nitroglycerine or pentaerythritol tetranitrate. The method was field tested at Umatilla Army Depot and found to provide a simple, rapid method for estimating TNT concentrations in the field. Concentration estimates from field analysis correlated well with laboratory analyses of the same samples.

14. SUBJECT TERMS

Explosives	Groundwater pollution	TNT
Field analysis methods	Soil contamination	

15. NUMBER OF PAGES: 24

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18
298-102